

WHAT IS CLAIMED IS:

1. A method of inhibiting fouling of heat transfer surfaces in contact with petroleum or hydrocarbon feedstocks comprising contacting the heat transfer surfaces with an effective amount of a thermally-treated phosphorous-sulfur compound.
2. The method of claim 1 wherein the fouling is coke formation in pyrolysis furnaces during thermal cracking of hydrocarbon feedstock.
3. The method of claim 1 wherein the thermally-treated phosphorous-sulfur compound is prepared by heating a phosphorus-sulfur compound at a temperature of from about 160° to about 500 °C.
4. The method of claim 3 wherein the phosphorus-sulfur compound is selected from mono- or di-substituted thiophosphate esters, phosphorothioites, phosphorothioates and thiophosphonates.
5. The method of claim 4 wherein the phosphorus-sulfur compound is a trisubstituted phosphorothioate.
6. The method of claim 5 wherein the trisubstituted phosphorothioate is a s,s,s-trialkyl phosphorothioate.
7. The method of claim 6 wherein the s,s,s-trialkyl phosphorothioate is s,s,s-tributyl phosphorothioate.
8. The method of claim 4 wherein the phosphorus-sulfur compound is a mono- or di-substituted thiophosphate ester.

9. The method of claim 8 wherein the mono- or di-substituted thiophosphate ester is a mono- or di-alkyl thiophosphate ester.

10. The method of claim 9 wherein the mono- or di-alkyl thiophosphate ester is mono- or dioctyl thiophosphate ester or mono- or di(ethyl)hexyl thiophosphate ester.

11. The method of claim 3 wherein the thermally-treated phosphorous-sulfur compound is prepared by heating a phosphorus-sulfur compound at a temperature of from about 180° to about 280 °C.

12. The method of claim 3 wherein the thermally-treated phosphorous-sulfur compound is prepared by heating a phosphorus-sulfur compound at a temperature of from about 200° to about 260 °C.

13. The method of claim 3 wherein the phosphorous-sulfur compound is heated in an oxygen and water-free atmosphere.

14. The method of claim 2 comprising injecting the thermally-treated phosphorous-sulfur compound into the pyrolysis furnace prior to processing the hydrocarbon feedstock.

15. The method of claim 14 wherein the thermally-treated phosphorous-sulfur compound is injected into the pyrolysis furnace from about 30 minutes to about 24 hours prior to processing the hydrocarbon feedstock.

16. The method of claim 2 comprising injecting the thermally-treated phosphorous-sulfur compound into the pyrolysis furnace simultaneously with hydrocarbon feedstock.

17. The method of claim 2 comprising injecting from about 1 to about 1000 ppm of the thermally-treated phosphorus-sulfur compound into the pyrolysis furnace.

18. The method of claim 2 comprising injecting from about 10 to about 100 ppm of the thermally-treated phosphorus-sulfur compound into the pyrolysis furnace.

19. A method of injecting a thermally-treated phosphorus-sulfur compound into a pyrolysis furnace coil comprising pumping a phosphorus-sulfur compound through a microthermal reactor, wherein the microthermal reactor is heated such that the effluent from the microthermal reactor comprises thermally-treated phosphorous-sulfur compound, and injecting the thermally-treated phosphorous-sulfur compound into the pyrolysis furnace coil.

20. The method of claim 19 wherein that the effluent from microthermal reactor has a temperature of from about 200 °C to about 500 °C.

21. The method of claim 19 further comprising mixing the phosphorous-sulfur compound or the thermally-treated phosphorous sulfur with a carrier.

22. The method of claim 21 wherein the carrier is a gas or a liquid.

23. The method of claim 21 wherein the carrier is steam.

24. The method of claim 21 wherein the carrier is an inert gas.

25. The method of claim 24 wherein the carrier is nitrogen.

26. The method of claim 21 wherein the carrier is natural gas.

27. An apparatus for injecting a thermally-treated phosphorus-sulfur compound into a pyrolysis furnace coil comprising means for pumping a phosphorus-sulfur compound through a microthermal reactor in which the phosphorous-sulfur compound is converted to the thermally-treated

phosphorous-sulfur compound and means for introducing the thermally-treated phosphorous-sulfur compound effluent from the microthermal reactor into the pyrolysis furnace coil.

28. The apparatus of claim 27 wherein the microthermal reactor is a continuous-flow reactor equipped with a heating device.

29. The method of claim 27 wherein the microthermal reactor is heated by steam.

30. The apparatus of claim 27 wherein the heating device is the pyrolysis coils at the crossover from convection to radiant sections of a pyrolysis furnace.

31. The apparatus of claim 27 wherein the heating device is the fire box of a pyrolysis furnace.

32. The apparatus of claim 27 wherein the heating device is an electrical heater.

33. The apparatus of claim 27 further comprising means for mixing the phosphorous-sulfur compound or the thermally-treated phosphorous-sulfur compound with a carrier.